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(54) WATER-SOLUBLE POLYAMMONIUM  
COMPOUNDS

(71) We, AKADEMIE DER WISSENSCHAFTEN DER DDR, of 5, Rudower Chaussee, 1199 Berlin, German Democratic Republic, a Corporation organised under the laws of the German Democratic Republic, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with high molecular weight, water-soluble polyammonium compounds and with the preparation thereof.

More particularly, the present invention is concerned with branched and/or partly cross-linked high molecular weight, water-soluble polymers of diethylenically-unsaturated ammonium monomers with cross-linking-acting co-components and with a process for the preparation of branched and/or partly cross-linked, water-soluble copolymers of diethylenically-unsaturated dialkyl ammonium monomers with cross-linking-acting co-components.

The compounds according to the present invention are useful, for example, as flocculation agents, sludge conditioning agents, anti-static agents and electrically-conductive paper coating materials.

It is generally known that the useful properties of water-soluble synthetic polymers and co-polymers of diethylenically-unsaturated ammonium monomers, when used, for example, as flocculation agents, coagulation agents, sludge conditioning agents, friction-reducing agents, antistatic agents and electrically-conductive paper coating materials, improve with increasing molecular weight, the resulting molecular weight of the polymers and copolymers, which are prepared by radical polymerisation in aqueous solution, depending upon the degree of purity of the monomers employed, upon the choice of the initiator system, upon the concentration of the monomers and of the initiators and upon the speed of decomposition of the initiator. It is also known that these diethylenically unsaturated ammonium compounds can be homopolymerised by radical initiation with appropriate initiators, for example ammonium persulphate, hydrogen peroxide, organic peroxide compounds, diazo compounds or redox systems, to give water-soluble linear polyammonium salts and can be co-polymerised with mono-functional or cross-linking co-monomers, the polymerisation reactions being carried out with oxygen-free monomer solutions under an inert gas atmosphere since, in principle, oxygen reacts with free radicals and thus the polymerisation can be inhibited.

According to U.S. Patent Specification No. 3,472,740, water-soluble homopolymers of dimethyl diallyl ammonium chloride are obtained by a process in which polymerisation is initiated by thermal decomposition of ammonium persulphate under an atmosphere of nitrogen.

U.S. Patent Specification No. 3,639,208 discloses that linear, water-soluble copolymers of dimethyl diallyl ammonium chloride (hereinafter referred to as DMDAAC) with acrylamide can be obtained by radical polymerisation at 50°C when the monomer solution is freed from dissolved oxygen by flushing with nitrogen and the reaction takes place under an atmosphere of an inert gas, the

polymerisation being initiated by the redox system ammonium persulphate-sodium metabisulphite.

According to U.S. Patent Specification No. 3,544,318 and French Patent Specification No. 1,494,438, very high molecular weight cross-linked co-polymers of diethylenically unsaturated dialkyl ammonium halides are obtained with certain cross-linking components, such as methylene bis-acrylamide, tetraallyl ammonium chloride and triallylamine hydrochloride, according to a preferred embodiment of the process according to U.S. Patent Specification No. 3,472,740. Here, too, radical polymerisation takes place with the exclusion of oxygen.

Additional requirements are demanded of water-soluble, synthetic polymers which are to be employed for the production of electrically-conductive paper coatings. Amongst other things, they must have a sufficient degree of conductivity over a wide range of relative atmospheric humidity and, in addition, only have a low penetration into the base paper and protect the coated paper, by a barrier effect, against penetration by solvents in the case of subsequent coating with a photoconductive layer. These properties can be achieved when, to the solution of the initial monomers in water, there are added high functional, cross-linking, soluble co-monomers such as methylene bisacrylamide, tetraalkylammonium chloride and trialkylamine hydrochloride, in such amounts that, after polymerisation has taken place, a branched and/or partly cross-linked, water-soluble polymer is obtained. As is generally known, the molecular weight of the polymer, in comparison with polymerisation without the addition of higher functional cross-linking soluble co-monomers, is thereby increased.

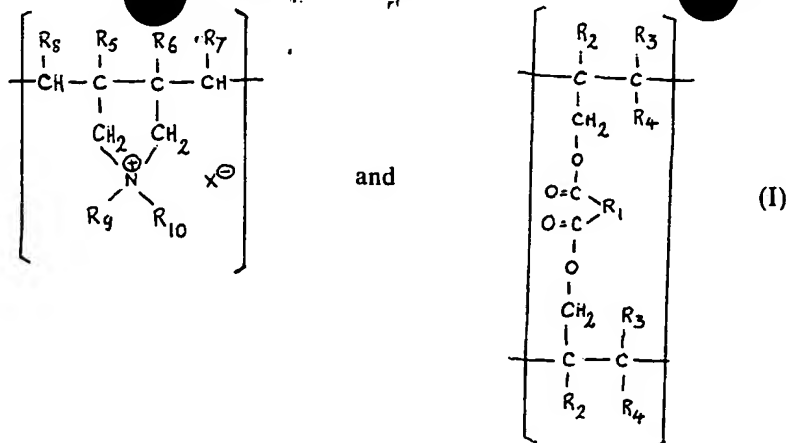
If, now, there are used the previously known and above-described co-polymers of diethylenically unsaturated ammonium monomers and the above-mentioned water-soluble, polyfunctional, cross-linking co-monomers for the production of electrically conductive paper coatings, then these polymers do not display the desired technical working up properties which permit an uncomplicated coating with the paper coating materials, as well as further working up of the coated paper. Thus, in the production of the electrically conductive papers, in the case of coating with the paper coating material, high application weights are necessary due to the flow properties of the coating material. Furthermore, the so-obtained electrically-conductive papers have a disadvantageous stickiness which leads to sticking of the paper rolls, depositions and papers tears in the case of further working up.

It is an object of the present invention to provide branched and/or partly cross-linked, water-soluble poly-ammonium compounds by the co-polymerisation of diethylenically unsaturated dialkyl ammonium monomers, preferably of DMDAAC, with particular polyfunctional, cross-linking co-monomers which, in comparison with the known copolymers, are products which, especially in the case of the production of electrically-conductive papers, display more favourable technical working up properties, i.e. they ensure an uncomplicated coating with the paper coating materials, as well as an uncomplicated further working up of the so-obtained electrically-conductive papers.

A further object of the present invention is provide a more economic process for the copolymerisation of diethylenically-unsaturated ammonium compounds, for example of DMDAAC, with polyfunctional cross-linking comonomers in aqueous solution which gives co-polymers with high molecular weights which can be used, for example, as flocculation agents, antistatic agents, electrically-conductive paper coating materials, sludge-conditioning agents, textile finishing agents, coagulation agents and friction-reducing agents.

The problem forming the basis of the present invention is to provide new polymers with specific properties as conductive polymers by the co-polymerisation of diethylenically-unsaturated dialkyl ammonium compounds with sparingly water-soluble or water-insoluble co-monomers and to provide an economic process for the co-polymerisation of diethylenically-unsaturated ammonium compounds with these polyfunctional cross-linking co-monomers.

We have found that water-soluble, high molecular weight, branched and/or partly cross-linked co-polymers composed of units of the general formulae:—



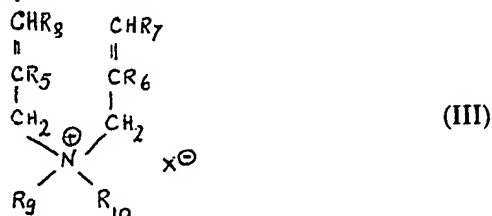
wherein  $R_1$  is a divalent  $-(CH_2)_x-$ ,  $-(CH=CH)_y$  or  $-(O-CH_2-CH_2)_z-O-$  radical or a divalent arylene radical or a divalent, substituted or unsubstituted cycloalkylene radical,  $x$  is 0 or 1 to 20,  $y$  is 1 to 4 and  $z$  is 0 or 1 or 5,  $R_2$ ,  $R_3$  and  $R_4$ , which may be the same or different, are hydrogen atoms or alkyl radicals containing up to 6 carbon atoms or cycloalkyl radicals containing 5 or 6 carbon atoms or aryl radicals,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$ , which can be the same or different, are hydrogen atoms or alkyl radicals containing up to 6 carbon atoms,  $R_9$  and  $R_{10}$ , which can be the same or different, are alkyl radicals containing up to 18 carbon atoms or aryl or benzyl radicals and  $X^\ominus$  is a halide, nitrate, hydroxide, hydrogen sulphate or dihydrogen phosphate ion, are obtained from diethylenically-unsaturated dialkyl ammonium salts, of general formula (III), preferably DMDAAC, when, for the co-polymerisation in water, there are used, as polyfunctional, cross-linking co-monomers, the hereinafter defined sparingly water-soluble or water-insoluble compounds of general formula (II), without further additives.

As multiple ethylenically-unsaturated, cross-linking co-monomers, there are used compounds of the general formula:—



wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  have the same meanings as above.

As diethylenically-unsaturated dialkyl ammonium compounds, there are used compounds of the general formula:—



wherein  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$  and  $X^\ominus$  have the same meanings as above.

In the case of the radical co-polymerisation of the above-described diethylenically-unsaturated dialkyl ammonium compounds (III) with 0.01 to 5 mole % of one or more of the multiple ethylenically-unsaturated, cross-linking co-monomers (II), there are obtained high molecular weight, water-soluble branched and/or partly cross-linked co-polymers which are outstandingly suitable for the production of electrically conductive paper coatings. Only small application weights of the coating material are necessary in order to produce electrically-conductive papers which display a sufficient conductivity over a wide range of relative atmospheric humidities. The coated, electrically-conductive papers do not display any stickiness so that an uncomplicated further working up of these papers is possible.

As initiators of the co-polymerisation of compounds (III) with polyfunctional co-monomers (II), there can be used those compounds which are capable of forming free radicals, for example water-soluble persulphates inorganic and

organic peroxides and azo compounds. As starter for the polymerisation, there can also be used a redox system, especially when it is desired to carry out the polymerisation at a relatively low temperature, preferably between 10 and 50°C. Conventional redox systems include, for example, sodium metabisulphite-potassium or ammonium persulphate-ferrous or cupric salts, the persulphate-ascorbic acid system, the persulphate-lithium bromide system and the permanganate-oxalic acid system.

We have also found that water-soluble, high molecular weight branched and/or partly cross-linked co-polymers are formed from diethylenically-unsaturated dialkyl ammonium compounds, preferably from DMDAAC, which are very suitable for the above-mentioned fields of use, when working under the influence of the external atmosphere insofar as the initiator concentration and/or the concentration of the chelating agent is increased and/or an increased temperature is used, as well as when the cross-linker concentration is possibly increased in comparison with the preferred embodiments of the already known processes in which polymerisation takes place in the absence of oxygen.

Consequently, according to a preferred embodiment of the present invention, water-soluble, high molecular weight branched and/or partly cross-linked copolymers of compounds of general formulae (II) and (III) are obtained by preparing an aqueous solution of the monomers, which solution contains 10 to 80% by weight of monomer of general formula (III) and 0.01 to 5 mole% of comonomer (II), adding a chelating agent in an amount of from  $5 \times 10^{-5}$  to  $5 \times 10^{-2}$  mole per mole of monomer, adjusting the temperature of the monomer solution to about 10 to 115°C or, under inert conditions, to 50 to 100°C, adding the initiator continuously in an amount of from  $10^{-3}$  to  $10^{-1}$  mole per mole of monomer and allowing the polymerisation to proceed isothermally or adiabatically.

The following Examples are given for the purpose of illustrating the present invention:

#### Example 1

Into a 40 litre reaction vessel, which is equipped with a mechanical stirrer, an inert gas flushing tube, thermometer, reflux condenser and heating means, there are placed 24.0 kg. of a 50% by weight aqueous solution of DMDAAC. To this solution is added 1.52 g (200 ppm) disodium dihydrogen ethylenediaminetetraacetate dihydrate, as well as 72.8 g (0.5 mole %) diallyl maleate. The solution is heated to 50°C and flushed with nitrogen. Subsequently, an initiator solution of 322 g ammonium persulphate in 2.0 litres water is added uniformly, in the course of 100 minutes and under an inert gas atmosphere to the solution of the monomers. When the addition of the initiator is completed, the co-polymer solution, which has, in the meantime, become viscous, is maintained for a further hour at about 100°C. The aqueous co-polymer solution thus obtained can be used directly for the production of coating masses for paper coating in the production of electrically conductive papers. For the production of electrically-conductive papers which, over a wide range of relative atmospheric humidity, display a sufficient conductivity, only small amounts by weight of applied material of the coating mass are necessary. The coated, electrically conductive papers no longer display any stickiness so that an uncomplicated further working up of these papers is possible.

#### Example 2

7.6 kg of a 50% by weight DMDAAC solution (24.5 mole) are placed in an appropriate polymerisation apparatus, together with 48.8 g tartaric acid (0.325 mole), warmed to 35°C and the apparatus flushed with nitrogen. After the addition of 54.75 g sodium disulphite (0.29 mole) 2.1 g ferrous ammonium sulphate ( $5 \times 10^{-3}$  mole) and 58.2 g diallyl fumarate (0.4 mole %), there is continuously pumped in, over the course of 70 minutes, a 0.5 molar solution of ammonium persulphate at a rate of 11.5 ml per minute. The aqueous copolymer solution thus obtained can be used directly for the production of coating masses for paper coating in the case of the production of electrically-conductive papers. For the production of electrically-conductive papers which display a sufficient conductivity over a wide range of relative atmospheric humidity, only small amounts by weight of the coating mass are necessary. The coated, electrically-conductive papers display no stickiness so that an uncomplicated further working up of these papers is possible.

#### Example 3

7.6 kg 50% by weight DMDAAC solution (24.5 mole) are placed in an appropriate polymerisation apparatus, together with 48.8 g tartaric acid (0.325

mole) and warmed to 40°C. After the reaction mixture has been mixed with 95 g sodium metabisulphite (0.5 mole), 2.1 g ferrous ammonium sulphate ( $5 \times 10^{-3}$  mole) and 106 g diallyl fumarate (0.8 mole %), a 1 molar solution of ammonium persulphate is added continuously, while stirring, over a period of time of 50 minutes at a rate of 10 ml per minute. The polymer solution thus obtained is, in its properties, comparable with co-polymers which have been obtained by co-polymerisation under an inert gas with a reduced concentration of cross-linker (0.5 mole % diallyl fumarate) and initiator concentration (0.29 mole disulphite and 0.29 mole persulphate), under otherwise the same conditions, and is outstandingly suitable for use as a conductive resin for electrically-conductive papers.

#### Example 4

50 g of a 50% by weight DMDAAC solution and 680 mg diallyl terephthalate (1.5 mole %), 318 mg tartaric acid ( $2.1 \times 10^{-3}$  mole), 620 mg sodium disulphite ( $3.3 \times 10^{-3}$  mole) and 13 mg ferrous ammonium sulphate ( $3.3 \times 10^{-5}$  mole) are warmed to 40°C in an appropriate polymerisation apparatus. To this there are continuously dosed in 764 mg ammonium persulphate ( $3.35 \times 10^{-3}$  mole), dissolved in 10 ml water, within the course of 100 minutes. For the isolation of the polymer, the polymer solution can be precipitated by pouring the aqueous solution into a non-solvent therefor, for example acetone. The white, scarcely hygroscopic co-polymer, obtained in quantitative yield, when dissolved in 1N aqueous sodium chloride solution, has, at 30°C., a limiting viscosity which is about 100% higher than the limiting viscosity of the homopolymer of DMDAAC obtained under the same conditions.

#### Example 5

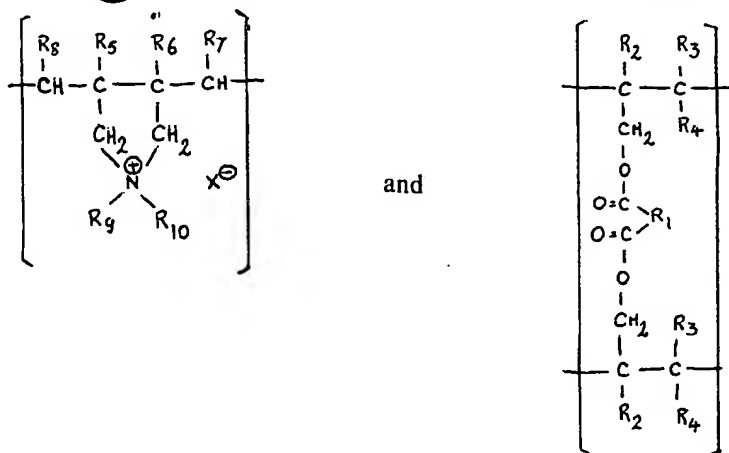
50 g of a 50% by weight aqueous DMDAAC solution are co-polymerised with 470 mg diallyl cyclohexane-dicarboxylate (1 mole%) in a polymerisation apparatus of the kind used in Example 4. The aqueous co-polymer solution is poured into acetone to give an almost quantitative yield of white, scarcely hygroscopic, water-soluble co-polymer which, in 1N aqueous sodium chloride solution, has a limiting viscosity, measured at 30°C, which is about 100% higher than the limiting viscosity of the polymer of DMDAAC obtained under the same conditions but without the addition of the co-monomer. The polymer solution thus obtained is, in its properties, comparable with co-polymers obtained by the co-polymerisation, under an inert gas, with reduced cross-linker concentration (0.4 mole% diallyl fumarate) and initiator concentration (0.29 mole disulphite and 0.29 mole persulphate) under otherwise the same conditions and is outstandingly suitable for use as a conductive resin for electrically-conductive papers.

#### Example 7

50 g of 50% by weight dimethyl diallyl ammonium chloride solution are mixed, in an appropriate polymerisation apparatus, with 200 ppm disodium dihydrogen ethylenediamine-tetraacetate dihydrate (EDTA) and 200 mg diallyl malonate and warmed to 95°C. To this there are continuously dosed in 900 mg ammonium persulphate ( $3.95 \times 10^{-3}$  mole) in 10 ml water, within the course of 100 minutes. Thereafter, the polymer solution is maintained for about 30 minutes at about 100°C. In order to isolate the polymer, the polymer solution can be diluted with water and the polymer precipitated out by pouring the aqueous solution into a non-solvent, for example acetone. The polymer, obtained in quantitative yield, has, in 1N aqueous sodium chloride solution at 30°C, the same limiting viscosity as a polymer which has been obtained according to the previously usual manner of working by polymerisation under an inert gas atmosphere with the use of a somewhat reduced amount of initiator and chelating agent (for example 764 mg peroxide disulphate and 100 ppm ethylenediamine-tetraacetic acid. The polymer solution thus obtained is, in its properties, comparable with co-polymers which have been obtained by co-polymerisation under an inert gas with a reduced cross-linker concentration (0.4 mole diallyl fumarate) and initiator concentration 0.29 mole disulphite and 0.29 mole persulphate) under otherwise the same conditions and is outstandingly suitable for use as a conductive resin for electrically conductive papers.

#### WHAT WE CLAIM IS:—

1. High molecular weight, water-soluble polyammonium compounds composed of units of the general formulae:—



wherein  $R_1$  is a divalent  $-(CH_2)_x-$ ,  $-(CH=CH)_y$  or  $-(O-CH_2-CH_2)_z-O-$  radical or a divalent arylene radical or a divalent, substituted or unsubstituted cycloalkylene radical,  $x$  is 0 or 1 to 20,  $y$  is 1 to 4 and  $z$  is 0 or 1 to 5,  $R_2$ ,  $R_3$  and  $R_4$ , which may be the same or different, are hydrogen atoms or alkyl radicals containing up to 6 carbon atoms or cycloalkyl radicals containing 5 or 6 carbon atoms or aryl radicals,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$ , which can be the same or different, are hydrogen atoms or alkyl radicals containing up to 6 carbon atoms,  $R_9$  and  $R_{10}$ , which can be the same or different, are alkyl radicals containing up to 18 carbon atoms or aryl or benzyl radicals and  $X^\ominus$  is a halide, nitrate, hydroxide, hydrogen sulphate or dihydrogen phosphate ion.

2. Polyammonium compounds according to claim 1, which are hereinbefore specifically exemplified.

3. Process for the production of high molecular weight, water-soluble polyammonium compounds from water-soluble diethylenically-unsaturated dialkyl ammonium compounds, co-monomers and an initiator, wherein 0.01 to 5 mole%, referred to the monomeric dialkyl ammonium compound, of at least one sparingly water-soluble or water-insoluble polyfunctional cross-linking co-monomer of the general formula:—



in which  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  have the same meanings as in claim 1, is added to a 10 to 80% by weight solution of a diethylenically-unsaturated dialkyl ammonium compound of general formula (III), and co-polymerised in the presence of an initiator in an inert atmosphere at a temperature of from 50 to 100°C.

4. Process for the production of high molecular weight, water-soluble polyammonium compounds from water-soluble diethylenically-unsaturated dialkyl ammonium compounds with a co-monomer of general formula (III) given in claim 3 in a redox system, wherein 0.01 to 5 mole%, referred to the monomeric dialkyl ammonium compound, of at least one sparingly water-soluble or water-insoluble polyfunctional, cross-linking co-monomer of general formula (II) given in claim 3, is added to a 10 to 80% by weight aqueous solution of the diethylenically-unsaturated dialkyl ammonium compound of general formula (III) and in the presence of a redox system, the reduction agent first being prepared and the oxidation agent dosed in co-polymerisation being carried out in an inert atmosphere at a temperature of from 10 to 50°C.

5. Process for the production of high molecular weight, water-soluble polyammonium compounds by co-polymerisation of water-soluble diethylenically-unsaturated dialkyl ammonium compounds with polyfunctional, cross-linking co-monomers in the presence of an initiator, wherein an aqueous solution of the diethylenically-unsaturated dialkyl ammonium compound of general formula (III), is polymerised with 0.01 to 5 mole%, referred to the monomeric dialkyl ammonium compound, of at least one sparingly water-soluble or water-insoluble polyfunctional, cross-linking co-monomer of general formula (II) given in claim 3, with the addition of a polymerisation initiator in a concentration of  $10^{-3}$  to  $10^{-1}$  mole per mole of monomer and with the addition of a chelating agent in a concentration of from  $5 \times 10^{-5}$  to  $5 \times 10^{-2}$  mole per mole of monomer in the presence of atmospheric oxygen, in aqueous solution at a temperature of from 10 to 115°C.

6. Process according to any of claims 3 to 5, wherein the polyfunctional, cross-linking co-monomer used is diallyl maleate, diallyl fumarate or ethylene glycol bis-allyl carbonate.

5 7. Process according to claim 4, wherein the redox system used is an ammonium persulphate-sodium metabisulphate system in a ratio of 1:1 to 1:0.5 in a concentration of from  $10^{-3}$  to  $5 \times 10^{-2}$  mole per mole of monomer and ferrous ammonium sulphate in a concentration of 100 to 300 ppm. 5

8. Process according to claim 7, wherein the ammonium persulphate-sodium metabisulphite system is used in a ratio of 1:0.75.

10 9. Process according to any of claims 4, 5 and 6, wherein a chelating agent is added to the system in an amount of from  $5 \times 10^{-5}$  to  $5 \times 10^{-2}$  mole per mole of monomer. 10

10. Process according to claim 9, wherein the chelating agent is tartaric acid, citric acid or phosphoric acid.

15 11. Process according to claim 3 or 5, wherein the polymerisation initiator is a peroxide compound. 15

12. Process according to claim 11, wherein the peroxide compound is ammonium persulphate or an alkali metal persulphate.

20 13. Process according to claim 4, wherein the polymerisation initiator is the redox system ammonium persulphate-sodium metabisulphite, optionally with a catalytic amount of a heavy metal salt or ammonium persulphate-lithium bromide, the redox agent first being prepared and the oxidation agent added thereto. 20

25 14. Process according to any of claims 3 to 13 for the production of polyammonium compounds substantially as hereinbefore described and exemplified. 25

15. Polyammonium compounds, whenever produced by the process according to any of claims 3 to 14.

30 16. Flocculation agents, antistatic agents, textile finishing agents, sludge conditioning agents coagulation agents, friction-reducing agents and electrically-conductive paper coating materials, whenever containing a polyammonium compound according to any of claims 1, 2 and 15. 30

17. Paper, whenever coated with a material containing at least one polyammonium compound according to any of claims 1, 2 and 15.

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